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ORIGINAL PAPER



# Identification of iron-bearing minerals in basalts and pillow lavas of the Kaczawa Mountains using $^{57}$Fe Mössbauer spectroscopy

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**Abstract.** The Kaczawa Mountains along with the Kaczawa foothill comprise a complicated geological unit that is called the Kaczawa metamorphic (Sudetes, SW Poland). The aim of our work was to identify the iron-bearing minerals in samples of basalts and pillow lavas from the Kaczawa metamorphic using $^{57}$Fe Mössbauer spectroscopy. Based on the preliminary results, the $Fe^{3+}/Fe^{2+}$ ratio in the samples was determined.

**Keywords:** Kaczawa Mountains • Mössbauer spectroscopy • basalts • pillow lavas

## Introduction

The Kaczawa metamorphic is located in the Sudetes and covers an area of 700 km$^2$. The unit is built of igneous, metamorphic and sedimentary rocks from the Cambrian to the Neogene period. The geological structure is extremely complicated [1]. The unit is divided into two zones – the oldest and deepest one that includes rocks formed in the early Paleozoic era and the younger zone that lies over the first zone and is built from rocks of the Carboniferous to the Cretaceous period. Cenozoic (the Miocene Epoch) basalts occur between these two zones.

The Miocene basalt samples were collected from four locations – Wilcza Góra, Małe Organy Myśliborskie, Klecza and Czartowska Skała. Basalt is a mafic, extrusive igneous rock that was formed from the rapid cooling of basaltic lava exposed to the surface. Basalts generally contain plagioclase, pyroxene, olivine, hornblende and magnetite as important accessory mineral [2].

Pillow lavas were collected from two locations – Wąwóz Myśliborski and Wleński Gródek near Klecza. The pillow lavas contain characteristic pillow-shaped structures that are attributed to the extrusion of lava under the water of Carboniferous ocean floor. Pillow lavas are of a basaltic chemical composition [2].

## Materials and methods

The rock samples were crushed and powdered in an agate ball mill and then prepared in the shape of a thin disk absorber. The Mössbauer transmission spectra were recorded at room temperature using RENOM MsAa-3 spectrometer and linear arrangement of a $^{57}$Co/Rh source (50 mCi) absorber and de-

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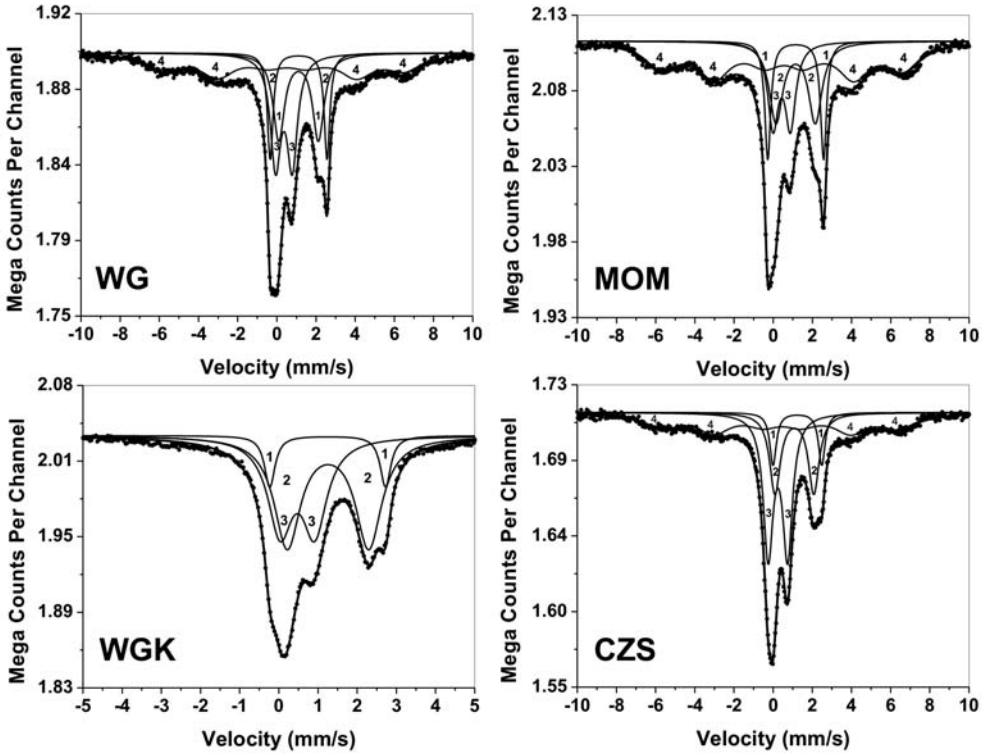


**Fig. 1.** $^{57}$Fe Mössbauer spectra at room temperature of basalt samples. Solid dots – experimental data; thick solid line – fitted curve; thin solid lines – fitted doublets and sextets.

tector (proportional counter). All Mössbauer spectra were numerically analysed using the Recoil software.

## Results and discussion

### Basalts

The Mössbauer spectra of the four basalt samples are shown in Fig. 1. The hyperfine parameters derived from the fitting procedure are given in Table 1. The Mössbauer spectra of basalts show doublets representing both $Fe^{2+}$ (labelled with no. 1 and no. 2 in Table 1) and $Fe^{3+}$ (labelled with no. 3) iron ions in octahedral coordination. The $Fe^{2+}$ doublets (no. 1, Fig. 1) with isomer shift (IS) values of 1.11–1.25 mm/s and quadrupole splitting (QS) of 2.5–3.0 mm/s are characteristic for olivine [3]. Olivine is a group of nesosilicate minerals that have the general formula of $(Mg,Fe)_2SiO_4$. The chemical composition of an olivine specimen falls between forsterite ($Mg_2SiO_4$) and fayalite ($Fe_2SiO_4$) [4]. The dominated $Fe^{2+}$ doublets with IS values of ~1.1–1.24 and QS ~ 2 mm/s (Table 1) can be assigned to augite

**Table 1.** Parameters for the $^{57}$Fe Mössbauer spectra (shown in Fig. 1) for investigated basalt samples. Isomer shift values are given relative to the α-Fe standard

| Sample | Line no. | $\chi^2$ | IS [mm/s] | QS [mm/s] | *B* [T] | Γ* [mm/s] | Valency | *A*** [%] | Mineral |
|---|---|---|---|---|---|---|---|---|---|
| Wilcza Góra (WG) | 1 | 1.1 | 1.11 | 2.90 | | 0.17 | $Fe^{2+}$ | 14 | Olivine |
| | 2 | | 1.10 | 2.02 | | 0.35 | $Fe^{2+}$ | 22 | Augite |
| | 3 | | 0.36 | 0.85 | | 0.32 | $Fe^{3+}$ | 26 | Hornblende |
| | 4 | | 0.44 | –0.07 | 38 | 1.05 | $Fe^{3+}$ | 38 | Goethite |
| Małe Organy Myśliborskie (MOM) | 1 | 1.8 | 1.14 | 2.85 | | 0.18 | $Fe^{2+}$ | 14 | Olivine |
| | 2 | | 1.14 | 2.00 | | 0.41 | $Fe^{2+}$ | 21 | Augite |
| | 3 | | 0.43 | 0.88 | | 0.32 | $Fe^{3+}$ | 17 | Hornblende |
| | 4 | | 0.50 | –0.04 | 38 | 1.00 | $Fe^{3+}$ | 48 | Goethite |
| Wleński Gródek near Klecza (WGK) | 1 | 1.6 | 1.25 | 3.00 | | 0.16 | $Fe^{2+}$ | 9 | Olivine |
| | 2 | | 1.24 | 2.08 | | 0.40 | $Fe^{2+}$ | 51 | Augite |
| | 3 | | 0.47 | 0.88 | | 0.38 | $Fe^{3+}$ | 40 | Hornblende |
| Czartowska Skała (CZS) | 1 | 1.4 | 1.24 | 2.50 | | 0.20 | $Fe^{2+}$ | 9 | Olivine |
| | 2 | | 1.09 | 1.98 | | 0.33 | $Fe^{2+}$ | 22 | Augite |
| | 3 | | 0.34 | 0.99 | | 0.30 | $Fe^{3+}$ | 34 | Hornblende |
| | 4 | | 0.42 | –0.05 | 37 | 1.00 | $Fe^{3+}$ | 35 | Goethite |

* Half width at half maximum. ** Relative contribution.

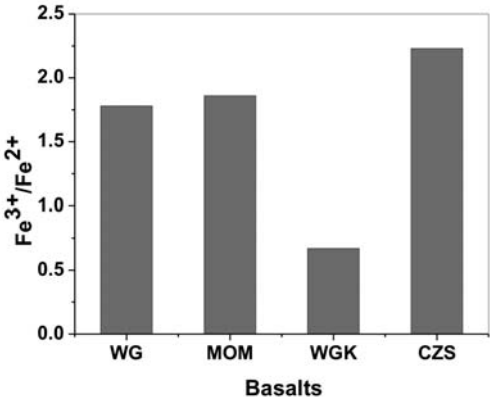


**Fig. 2.** $Fe^{3+}/Fe^{2+}$ ratio for investigated basalts.

$(Al,Ca,Fe,Mg,Ti)_2(Al,Si)_2O_6$. Augite is an essential mineral in basalts and belongs to the pyroxenes [2, 4]. Both olivine and augite were identified in all of the basalt samples. It is worth noting that similar components and contributions have been recorded in the spectrum of basalt from Wilcza Góra in the only paper dealing with Mössbauer spectroscopy in basalts from the Kaczawa Mountains [5].

According to the hyperfine parameters, $Fe^{3+}$ component (doublet no. 3), which is also identified in each basalt sample, most probably may be assigned to hornblende [3, 6]. Hornblende $(Ca,K,Na)_{2-3}(Mg,Fe^{2+},Fe^{3+},Al)_5(Si,Al)_8O_{22}(OH)_2$ represents the amphiboles that is an important group of inosilicate rock-forming minerals, which occur in igneous and metamorphic rocks [2, 4].

The visible difference in the spectra of basalts that were measured is connected with the magnetic fraction (no. 4, Fig. 1). A Zeeman sextet with magnetic field ($B$) of 38 T, was observed for WG, MOM and CZS samples. Based on the hyperfine parameters (Table 1), the magnetic phase can be unambiguously assigned to goethite – FeO(OH) [7]. Goethite is a common iron hydroxide in materials formed in the weathering environment. Consequently, the presence of goethite may be an indication of an early stage of the weathering process. On the other hand, goethite may be a result of hydrothermal processes during the formation of these basalts.

According to the hyperfine parameters listed in Table 1, a relatively high ratio of $Fe^{3+}/Fe^{2+}$ in the range of 1.8 to 2.2 is observed for WG, MOM and CZS basalts. It is due to the occurrence of goethite in these samples. If goethite is a result of the oxidation process, the high ratio of $Fe^{3+}/Fe^{2+}$ may reflect a stage of weathering. In WGK basalt, we have not observed goethite. Consequently, the $Fe^{3+}/Fe^{2+}$ ratio of 0.7 is lower than those calculated for other basalts (Table 1, Fig. 2).

## Pillow lavas

The Mössbauer spectra of the two pillow lava samples are shown in Fig. 3. The hyperfine parameters from the fitting procedure are summarized in Table 2. As can be seen in Fig. 3, despite the fact that both samples represent the same type of rock they show

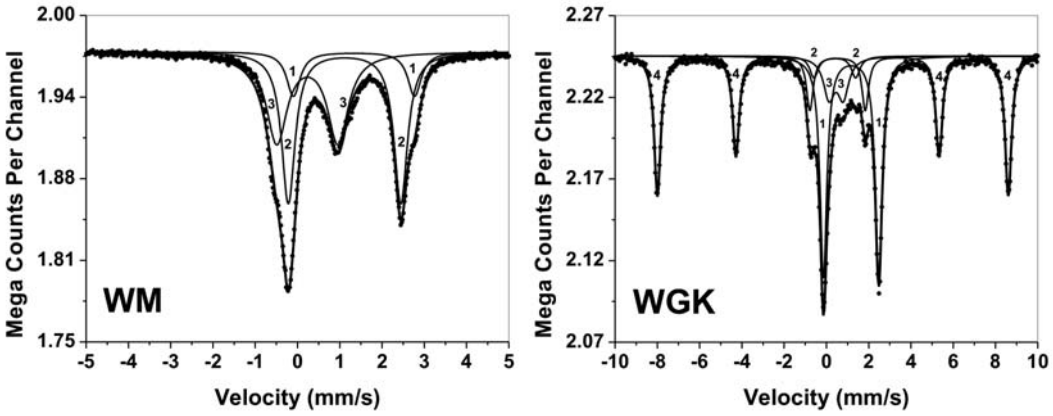


**Fig. 3.** $^{57}Fe$ Mössbauer spectra at room temperature of pillow lava samples. Solid dots – experimental data; thick solid line – fitted curve; thin solid lines – fitted doublets and sextet.

**Table 2.** Parameters for the $^{57}Fe$ Mössbauer spectra (shown in Fig. 3) for investigated pillow lava samples. Isomer shift values are given relative to the α-Fe standard

| Sample | Line no. | $\chi^2$ | IS [mm/s] | QS [mm/s] | $B$ [T] | Γ* [mm/s] | Valency | $A$** [%] | Mineral |
|---|---|---|---|---|---|---|---|---|---|
| Wąwóz Mysliborski (WM) | 1 | 1.2 | 1.11 | 2.60 | | 0.19 | $Fe^{2+}$ | 45 | Chlorite |
| | 2 | | 1.34 | 2.87 | | 0.19 | $Fe^{2+}$ | 15 | Hornblende |
| | 3 | | 0.23 | 1.45 | | 0.30 | $Fe^{3+}$ | 40 | Chlorite |
| Wleński Gródek near Klecza (WGK) | 1 | 1.6 | 1.17 | 2.61 | | 0.20 | $Fe^{2+}$ | 38 | Chlorite |
| | 2 | | 0.40 | 1.97 | | 0.24 | $Fe^{3+}$ | 4 | Ferrihydrite |
| | 3 | | 0.46 | 0.67 | | 0.31 | $Fe^{3+}$ | 11 | Chlorite |
| | 4 | | 0.42 | –0.11 | 52 | 0.19 | $Fe^{3+}$ | 47 | Hematite |

* Half width at half maximum. ** Relative contribution.

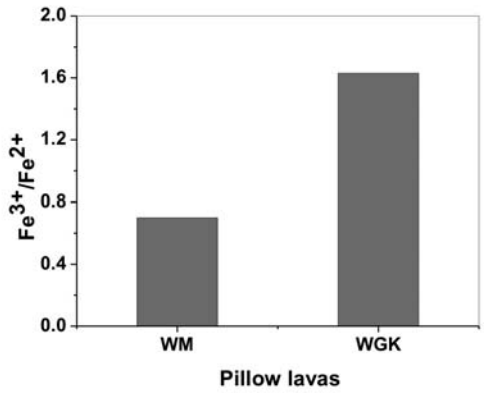


**Fig. 4.** $Fe^{3+}/Fe^{2+}$ ratio for investigated pillow lavas.

significant differences. The Mössbauer spectrum of the pillow lava from Wleński Gródek near Klecza (Fig. 3) is dominated by the sextet which can be unambiguously identified as hematite – $Fe_2O_3$ (labelled with no. 4 in Table 2). Hematite may be regarded as a secondary mineral in this type of rock and can be formed by the weathering of primary iron-bearing minerals or regional metamorphism [1, 5]. The presence of ferrihydrite $Fe_5(O_4H_3)_3$ (doublet no. 2) and hematite in the sample may be a result of advanced weathering.

The spectrum of the pillow lava sample from Wąwóz Myśliborski is characterized by the presence of two $Fe^{2+}$ doublets (Fig. 3) representing chlorite (no. 1) and hornblende (no. 2), and one $Fe^{3+}$ doublet (no. 3) also associated with chlorite [6, 8]. Chlorite $(Mg,Al,Fe^{2+})_{12}[(Si,Al)_8O_{20}](OH)_8$, a micaceous greenish mineral, is common in low-grade schist or as the alteration product of pyroxenes or amphiboles [5]. Chlorite phase was also identified in the WGK sample (doublets no. 1 and 3).

Surprisingly, unlike the WGK basalt, the sample of WGK lava from nearly the same location (Wleński Gródek near Klecza) is characterized by $Fe^{3+}/Fe^{2+}$ ratio of 1.6 (Fig. 4). It is a result of the occurrence of hematite in this sample; its contribution covers about 47% of the spectrum. In the WM sample, we have not observed hematite phase and the $Fe^{3+}/Fe^{2+}$ ratio is 0.7 (Fig. 4).

## Conclusions

Augite, olivine and hornblende phases were observed in all the Miocene basalts investigated. Using $^{57}Fe$ Mössbauer spectroscopy, magnetic phases associated with goethite and hematite were identified in basalts and pillow lava. The high ratio of $Fe^{3+}/Fe^{2+}$ determined by the Mössbauer measurements for three basalts is a result of the occurrence of goethite in these samples. The present work shows that $^{57}Fe$ Mössbauer spectroscopy is a useful method to identify iron-bearing minerals in igneous rocks. Such measurements of rock samples from other locations in the Sudetes are planned.

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